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TITLE: FUNDAMENTAL MECHANISMS OF OPTICAL DAMAGE IN SHORT-WAVELENGTH
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Fundamental Mechanisms Of Optical Damage In Short-Wavelength High-Power Lasers

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Evidence has been accumulating for many years that the physical mechanisms responsible for damage to optical materials in and from high-power, short-wave-length lasers (SWLs) differ in fundamental ways from the thermal processes identified in infrared and visible-wavelength laser damage problems. We propose that this difference stems primarily from the electronic nature of the absorption and excitation processes which occur when SWL photons strike an optical surface, and that electrons, ions and uv photons generated in the laser excitation cycle also contribute to optical damage. In this paper, we present recent experimental results which have pinpointed specific electronic excitation mechanisms which can operate in the high-power laser environment. In many optical materials of interest for SWLs, the deposition of electronic energy creates self-trapped excitons which decay through the energetic expulsion of atoms and molecules from the surface of the material. This erosion process is accompanied by the creation of permanent electronic defects which become nucleation sites for further damage. The relationship between these microscopic mechanisms and observed macroscopic damage phenomenology is discussed, along with evidence for the existence of a surface overlayer which may point the way to radically new techniques for protecting SWL optical elements from laser damage.

1. Introduction

Early studies of optical damage to laser components at wavelengths of 1 and 10 microns showed that there were two primary causes for catastrophic failure of large optical elements in higher power laser systems: first, the heating of submicron inclusions left from polishing or other manufacturing processes [1]; second, avalanche break-down or field emission at microcracks or pores in thin optical coatings [2]. These modes of laser damage have been studied for many years, and this work has brought significant improvements in the performance of optical materials, largely through improved quality control in the fabrication process. However, the very success of these explanations has also led to a strong predisposition to ascribe all optical damage either to thermal effects or to the excitation-energy density of high-power laser pulses, even in the face of experimental evidence that short-wavelength laser photons can induce physical and chemical transitions even in pure, structurally-perfect materials by multiphoton mechanisms [3].

We have been working to identify the fundamental damage limits for short-wavelength lasers set by physics and chemistry of the laser-materials interaction rather than by deficiencies in optical manufacturing practice. Our experimental techniques allow a significant degree of control over and characterization of the incident primary radiation, the substrates and overlayers chosen as model systems, and the dynamical state of atoms, ions and electrons ejected from the target materials following irradiation. Experiments based on these techniques are yielding an increasingly detailed picture of the ways in which microscopic absorption, localization and redistribution of absorbed photon and particle energy triggers macroscopic destructive events such as desorption, erosion, and ablation of optical surfaces.

Building on this evidence, we have argued elsewhere [4] that the primary damage mechanisms in short-wavelength lasers are electronic and that they are triggered not only by the laser light itself, but also by electrons and UV photons created in the pumping process and by excited ions and atoms in the laser gas plasma. This picture is consistent with recent experiments indicating the onset of a major change in the morphology of damage to selected dielectrics occurring somewhere in the wavelength region around 250 nanometers [5]. It is our contention that this damage mechanism can be identified with the onset of Desorption Induced by Electronic Transitions (henceforth DIET), a generic category of phenomena implicated in erosion and radiation

damage caused by low-energy electrons, protons and heavy particles (atoms, ions, etc.). Thus, we propose that the catastrophic failure modes of excimer laser optics are due to the DIET processes caused by ions, electrons and ultraviolet photons from the laser environment, as well as single- and multiple-photon desorption events induced by the laser photons. However, as we shall show, these electronically-induced desorption events also have thermal consequences, particular at laser flux levels above the plasma-formation limit.

In this paper, we first present experimental data from the Large-Aperture laser amplifier Module (LAM) at the Los Alamos National Laboratory, indicating the intensity of the various categories of radiation striking the optical surfaces. We next consider the ways in which DIET processes changes the surface composition and structure of model optical materials, keying our remarks both to specific electronic mechanisms and to the solid-state properties of alkali halides. We then discuss a model for damage-initiating events in a typical large excimer laser, in which not only the laser photons but also uv photons, electrons, ions and neutral atoms created by the laser pumping process can contribute to the destruction of optical surfaces. We shall make a plausibility argument supported by these data to demonstrate how initial low-fluence events induced by an electronic pre-cursors lead to changes in surface composition which result in catastrophic thermal breakdown when an intense laser pulse impinges on an optical surface. Finally, we adduce experimental evidence for the existence of a protective surface overlayer, the understanding of which may lead to a new class of damage-resistant coatings for short-wavelength lasers.

2. Sources Of Optical Damage In High-Power Excimer Lasers

Figure 1 shows a schematic of the Large-Aperture KrF laser amplifier Module (LAM) now operating at the Los Alamos National Laboratory, a device typical of current and planned large excimer lasers for fusion applications [6]. The LAM has an active volume of some 2 m³, and optical surfaces (resonator mirror and windows) exceeding 1 m² in size. A population inversion in an Ar-Kr-F₂ mixture is created through electronic excitation of the laser gas by two 400 kA beams of 750 KeV electrons from a cold cathode discharge. The electron trajectories in the gas are constrained to a direction transverse to the optical axis by a 4 kG magnetic field produced by a pair of large Helmholtz coils. The mirror and window have fused-silica or Pyrex substrates, typically coated with multi-layer dielectric thin films of SiO₂, Al₂O₃, or other metal halides or metal oxides.

The design fluence of the LAM is 1 J/cm² in a 500-ns pulse; large UV lasers now under design will produce laser fluences ranging up to several J/cm². The significance of these flux levels can be gauged by observing that, for a KrF laser (248 nm), 1 J/cm² corresponds to some 10¹⁶ photons per surface site on the irradiated optical elements. In electron-beam-pumped lasers, Bremsstrahlung X-rays produced by the deceleration of near-megavolt pump-beam electrons, as well as scattered or diffusing low-energy electrons, will also irradiate nearby optical surfaces. Each of these sources of radiation efficiently produces neutral atoms and molecules through DIET processes. Moreover, many low-energy ion species in the laser plasma--including oxygen, argon and fluorine--are known to be efficient at producing reactive-ion etching on insulators and semiconductors, particularly in the presence of uv radiation [7]. Thus, in the precursor phase of optical damage, both radiation from the laser environment and the laser photons themselves can play important roles.

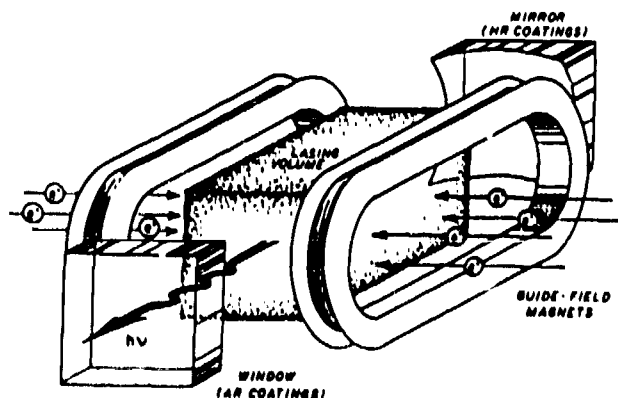


Fig. 1. Schematic of the Large-Aperture KrF Module at Los Alamos. Laser action is initiated by electron-beam pumping of a rare-gas halide mixture in the active volume.

Gross measurements of the radiation flux in the plane of the LAM exit window shows that, in spite of the large magnetic guide field, there is substantial leakage of the pump-beam electrons from the active laser volume to the optical surfaces of the chamber. In these experiments, a Faraday cup was placed in the center of the output window, a distance of approximately 40 centimeters from either electron beam cathode and the current was measured during repeated shots from one cathode. It was found that at this center position that the current flux of electrons ranged from 30 to 60 milliamperes per square centimeter. This gives an electron dose on the order of 10 to 100 electrons per surface site per shot. We also measured the total radiation dose at the window at several locations, using lithium fluoride thermal luminescence detectors, and discovered that the average is approximately 2 rads total dose per square centimeter per shot. Thus the laser environment contributes in a major way to optical damage, consistent with many anecdotal observations of dramatic reductions in damage threshold for optical materials "inside" high-power lasers.

3. Desorption Induced By Electronic Transitions in Optical Materials

The key to a fundamental understanding of optical damage in optical materials for SWLs is to find the link or links between the microscopic (i.e., atomic-scale) desorption of individual atoms or molecules from the optical material, and macroscopic erosion and large-scale surface damage. This requires dealing both with the detailed mechanisms of desorption and with the surface and solid-state properties of particular optical materials. The key questions revolve around the existence of certain decay channels through which incident energy may be transformed and redistributed to create defects and particle desorption. Hence, in contrast to thermal desorption processes--which depend only on the bulk thermodynamic properties of the optical material--any serious investigation of electronic desorption mechanisms must concern itself with the details of the optical material properties, such as band structure. In this section, we shall discuss DIET processes in a general way, and present representative experimental data used to obtain detailed dynamical information about them.

3.1. Electronically Stimulated Desorption of Neutral Atoms

DIET processes occur when low energy photons, electrons, ions or neutral atoms interact with the atoms in the surface and the near surface layer of bulk material. The DIET process as shown in Figure 2 is characterized by three stages: (1) an excitation stage in which the energy of the incoming particle or photon is deposited in the near-surface bulk; (2) the localization phase, lasting from 10^{-12} to 10^{-11} second, during which one or more atoms or molecules participating in the excitation arrives at an energy state which is on the repulsive part of the relevant potential energy surface; and (3) desorption, as the particle is actually expelled from the surface. During this last phase the particle may also undergo charge exchange or other electronic particle-surface interactions.

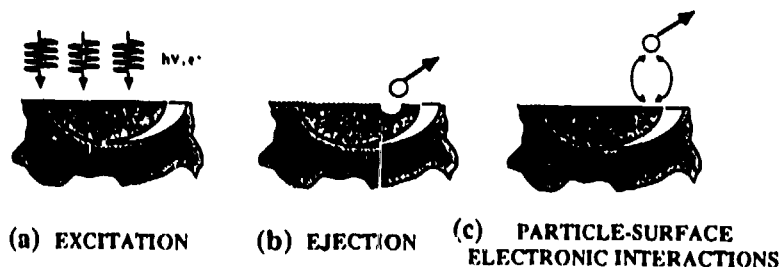


Fig. 2. Illustration of the three stages of a DIET process: (a) excitation; (b) localization of energy; and (c) desorption.

DIET spectroscopy or ions has been used for many years to obtain structural and compositional information on a variety of surfaces. Several mechanisms for ion DIET have been proposed, the first of which was the Menzel-Omer-Redhead model [8], devised to explain the desorption of adsorbed gases on metal surfaces. This model, characterized by the assumption that two-body gas-phase potentials can be used to explain the repulsive energy state, explains, in a qualitative way, the desorption of neutral adsorbates such as hydrogen from transition-metal surfaces. Beginning in the 1970's, Knotek and Feibelman devised a different mechanism to explain the desorption of ions from maximally valent covalent solids such as titanium dioxide [9]. In their model, the creation of long-lived hole pairs produces desorption via a Coulomb explosion. By demonstrating explicitly that the formation of hole pairs could increase the stability and lifetime of an

electronic excitation leading to desorption [10]. The role of specific solid-state properties of a select class of oxides in this process has been discussed [10]. The link between bond angles and desorption probabilities has been exploited by Madey, Yates and their coworkers to obtain detailed structural and compositional information about adsorbed species on both metal and insulator surfaces [11].

However, neither the Menzel-Gomer-Redhead nor Knotek-Felbman models are able to explain experiments showing conclusively that the DIET phenomenon in insulators (such as the alkali halides and alkaline earth halides) is overwhelmingly dominated by neutral particle production [12]. The predominance of neutral particle yields in electronically stimulated desorption means that in these materials ion desorption is largely irrelevant to studies of the fundamental dynamical mechanisms of desorption, simply because the largest fraction of absorbed energy goes into the production of neutral particles. We now consider representative results from neutral desorption spectroscopy in alkali crystals.

3.2. DIET Experiments on Single-Crystal Alkali Halides

The detection of neutral particles and the study of the desorption mechanism occurs primarily via optical techniques [13]. Figure 3 shows the schematic of a typical DIET experiment in which neutral particles either in the ground state or in the excited state desorbing from a surface are observed. The radiation source -- low energy photons, electrons or heavy particles -- is shown as incident from the left. The target surface, generally an insulator, is kept in a sample chamber under ultra-high vacuum, so that the formation of impurity adsorbates on the surface can be controlled or minimized. The target surface is mounted on a micromanipulator stage which can be heated or cooled to study temperature-dependent effects (e.g., defect migration) on desorption dynamics. When the radiation impinges on the target surface, desorption events occur and the desorbing particles begin to move away from the surface. Excited particles among the desorbing atoms and molecules radiate as free particles as they leave the surface. This radiation is detected by a spectrometer whose focal volume is arranged to intersect the volume of the exciting beam immediately in front of the target surface. It is this radiation which is detected by the spectrometer and which gives a characteristic optical signature of particle identity, internal energy state, velocity distribution and dependence on the state of the surface (e.g., temperature).

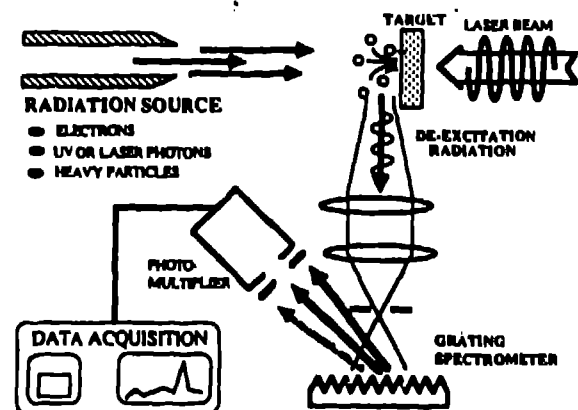


Fig. 3. Schematic of a DIET experiment using optical techniques to detect neutral atoms and molecules.

Ground-state particles leaving the surface, on the other hand, are detected by means of laser-induced fluorescence using a tunable dye laser beam, which is brought to a window in the ultra high vacuum chamber via a fiber-optic link. The light from the laser is collinear with and anti-parallel to the exciting beam so that the particles leaving the surface are excited by the laser into a state from which they can radiate via characteristic spectral lines. As an example, we consider the results of PSD experiments [14] of LiF single-crystal surfaces. The excitation source for these experiments was the Tantalus storage ring at the University of Wisconsin Synchrotron Radiation Center, with photons in the energy range from 40-200 eV.

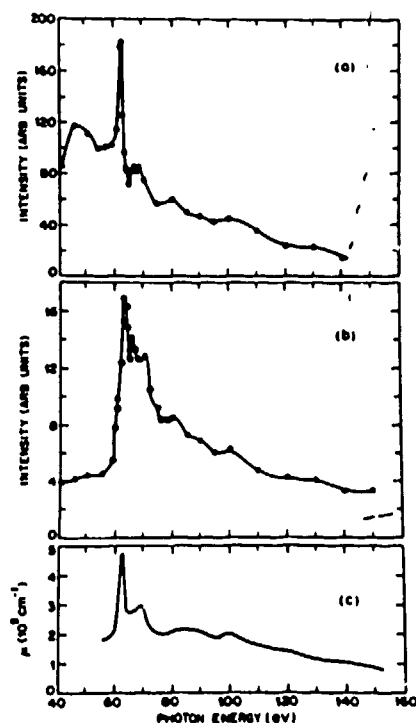


Figure 4 shows the optical emission intensity of (a) desorbed Li^* (excited Li atoms) as a function of the primary-beam photons, compared to the similar curve for (b) Li^+ (ions) and (c) the LIF photon absorption coefficient. In all three curves, the main excitonic structure of the Li K-edge is evident. Also, the high yield over a wide range of photon energies suggests that DIET processes are likely to remain efficient even down to relatively low energies, and certainly at energies characteristic of the electron-beam-produced Bremsstrahlung in a device such as the LAM. However, the most important feature of these curves is that the Li^* yield exceeds that of the Li^+ by five orders of magnitude. More recent measurements of the PSD yield of Li^0 (ground-state neutral lithium) showed that these yields exceed those of Li^* by one to two orders of magnitude.

Fig. 4. (a) PSD yield of Li^* from LIF.
(b) PSD yield of Li^+ from LIF.
(c) Optical transmission for LIF.

In the alkali halides following electron or photon impact, the halogen neutral atoms are ejected from the surface with a suprathermal energy, while the alkali neutrals are desorbed thermally.

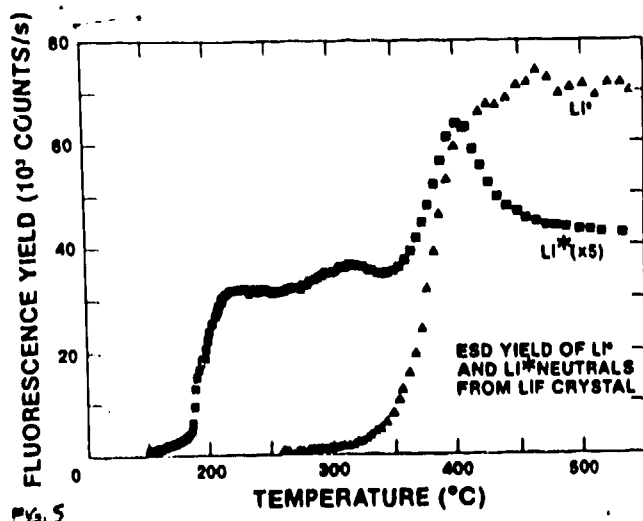


Fig. 5. Fluorescence yields of Li^0 and Li^* desorbed from single-crystal LIF, as a function of temperature.

Figure 5 shows the temperature dependence of the ESD yield of ground-state and excited-state lithium metal atoms from single-crystal lithium fluoride. The desorption yield curve for the ground state neutrals follows the classic Arrhenius desorption shape, increasing as a function of temperature until the yield of lithium metal atoms from the surface is equal to the rate at which they are being produced by the irradiating electrons. The excited state neutrals, on the other hand, are not desorbed thermally; there is other evidence suggesting that the Li^* are in fact not in thermal equilibrium with the surface at the moment of desorption. At temperatures below those required for desorption of either Li^0 or Li^* , then, there are microscopic agglomerations of free alkali metal on the surface of the irradiated alkali halide crystals - a situation fraught with significant implications for optical damage.

Collateral evidence for this picture of ESD/PSD in lithium fluoride comes from measurements from a variety of sodium halides showing that the velocities of desorbing ground-state sodium atoms have a Maxwellian distribution at the temperature of the surface. The number versus velocity distribution of the desorbing atoms is given by

$$dn/dv = Cv^2 \exp(-mv^2/2kT), \quad (1)$$

where the velocity v is related to the measured frequency ν of the emitted photons by the first-order Doppler formula

$$\nu = \nu_0 [1 + (v/c) \cos \theta]. \quad (2)$$

The parameter ν_0 is the central frequency for stationary atoms and θ is 0 in the geometry of these experiments. A frequency scan of the tunable dye laser around the characteristic ground-state absorption lines allows desorbing atoms to resonantly absorb laser light at the Doppler-shifted wavelength appropriate to their rest frame. The graph of fluorescence yield vs. frequency is thus equivalent to a scan of dn/dv .

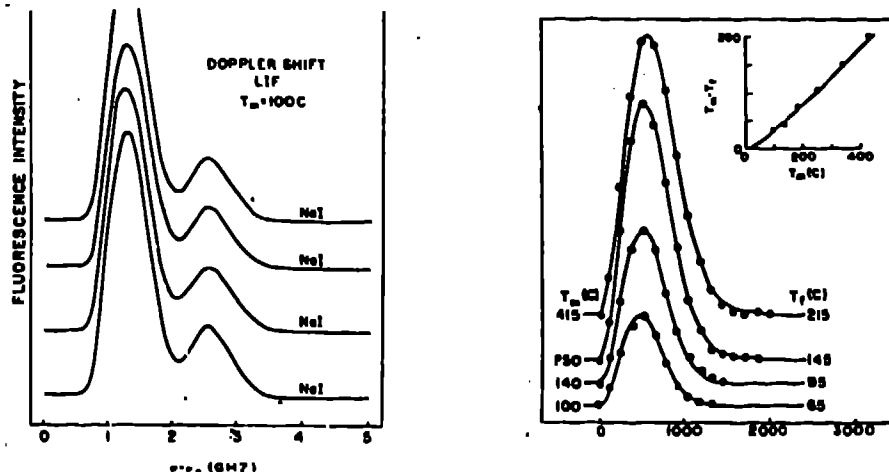


Fig. 6. (Left) Fluorescence yield as a function of laser-frequency for ground-state sodium desorbing from various sodium halides. (Right) Velocity distribution derived from the best-fit temperature for the measured Doppler-shifted frequency spectrum.

Figure 6 (Left) shows the measured data in the Doppler scanning configuration of the experiment on an Na-halide crystals, running over the two hyper-fine peaks of the Na D₂ line. Figure 6 (Right) compares the fitted Maxwell-Boltzmann temperatures with the measured surface temperatures over the range covered in one set of experiments. The measured surface temperature and the temperature inferred from the fitted velocity distributions differ by a constant amount, probably due to the gradient between the thermocouple probe and the surface. The measured surface and best-fit temperatures were and completely consistent with neutral ground-state alkalis desorbing in thermal equilibrium with the surface [15].

Some further clues to the character of the DIET mechanism in alkali halides come from time-resolved ESD measurements carried out on LiF. In these experiments, a chopped electron beam and a time-to-amplitude converter coupled to a multichannel analyzer were employed to measure the desorption yield in the "afterglow" period after the electron beam was turned off. Typical data for ground-state and excited-state neutrals at two different sample temperatures are shown in Figure 7. When the electron beam is turned off, the ground-state fluorescence yield decays slowly, indicating that thermally driven defects are migrating to the surface and reducing their free energy by triggering desorption events. The same kind of experiment has been carried out looking at the excited-state neutrals desorbed from lithium fluoride. But in this case, the yield of excited state neutral lithium exactly tracks the on-off pattern of the irradiating electron beam, indicating that there is no near-surface bulk contribution to the desorption yield; instead, the neutral excited lithium comes off the surface immediately as it is being irradiated. This shows that we are dealing with quite a different mechanism than that responsible for the desorption of ground state neutral lithium.

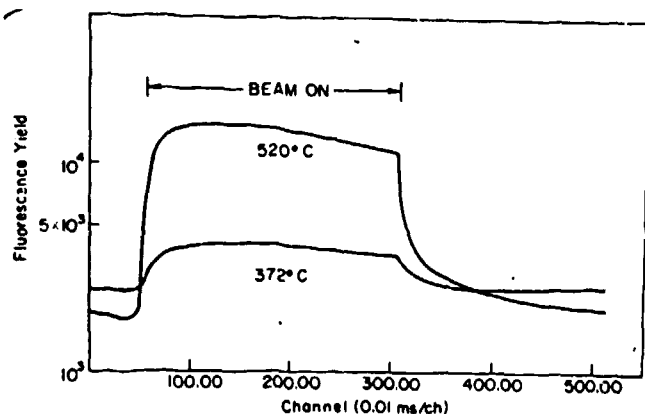


Fig. 7. Time dependence of yield for ground-state Li in ESD from LiF.

3.3. Mechanism for Ground-State Alkali Desorption

Summing up, one can say that electronically-stimulated desorption of ground-state alkalis from alkali halides exhibits features consistent with thermal desorption from the surface and near-surface bulk. In contrast, although the evidence is not so detailed as the results cited here for the alkalis, it has been shown that halogens desorbed from alkali halides under low-energy electron bombardment have suprathermal energies and are emitted in preferred directions along the halogen "strings" in the crystal. This suggests that the formation and relaxation of F-centers, as originally proposed by Pooley and Hersh [16], is a likely mechanism for the ejection of the halogens from the surface and near-surface layer of the bulk. The Pooley-Hersh model involves a specific electronic excitation leading to preferential and energetic ejection of halogens along the $\langle 110 \rangle$ directions (Fig. 9). Simultaneously, by leaving behind an electron to bind to the now undercoordinated alkali atoms near the surface, it provides a mechanism for the generation of neutral alkalis to undergo thermal desorption. Moreover, because the Pooley-Hersh mechanism is a simple one-step process--involving only the formation and relaxation of an exciton--the creation of neutral alkalis can occur relatively efficiently.

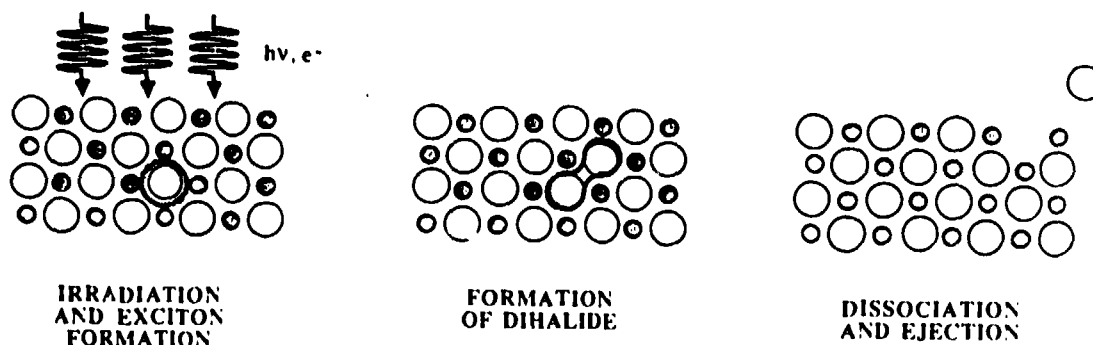


Fig. 8. Schematic of the Pooley-Hersh mechanism. The initial stage localizes the incident electronic energy through the creation of a self-trapped exciton. The transient dihalide molecular ion, formed by the overlap of the excited and a neighboring (normal) halogen ion, is in a predissociative state. When a halogen atom or ion is ejected preferentially along the halogen string directions, it leaves behind an F-center and a defect (halogen vacancy), allowing the undercoordinated alkali ion to be neutralized and desorb thermally.

With respect to optical damage in SWLs, the significance of the electronic precursor mechanism lies in the existence of free alkali metal atoms on the surface following electron or proton irradiation, as long as the surface remains sufficiently cold that thermal desorption does not occur. This implies, as we now discuss, a variety of undesirable consequences for optical materials generically related to the alkali halides.

4. Electronically-Induced Damage in Optical Dielectric Materials

From the microscopic point of view, electronically-induced damage in short wavelength optical materials arises from the ability of these dielectrics to store energy in a highly localized way and then to release that energy through destructive channels. The problem may be seen more clearly by contrasting the situation with that of a pure metal, in which the highly non-localized, conduction-band electrons are able to drain away incident energy from the absorption site and disperse it throughout the metal. In an insulator, such a dispersal of the incident energy is not easily possible, because of the tight binding of the valence-band electrons, reflected in the large size of band-gap energies for typical optical dielectrics. Moreover, in dielectrics there exist a variety of material dependent mechanisms-including exciton formation and the population of surface states-through which incident electronic energy can be localized in space and time sufficiently to trigger defect formation, desorption and other destructive events.

In this section, we discuss one possible scheme for analyzing the susceptibility of optical materials to damage based on generic materials properties. We also discuss evidence for the existence of an as yet uncharacterized overlayer on the surface of most materials, which appears to retard substrate desorption. Finally, we discuss a model of optical damage at short wavelengths, in which an electronic precursor mechanism changes the material composition and structure in ways which lead ultimately to catastrophic damage and failure of the material.

4.1. The Role of Specific Mechanisms

Early thermal models of optical damage were guided by an understanding of the interaction of infrared photons with the phonon spectrum of metals and insulators. Our picture of short wavelength optical damage we shall present is likewise guided by a recent characterization of electronic interactions in insulators and semiconductors due to Itoh [17]. This model of different classes of electronic materials allows us to relate experimentally observed desorption dynamics to specific materials properties. By concentrating on specific excitation mechanisms and on the dynamics of energy flow leading to desorption and, ultimately, erosion and material ablation, it is possible to correlate the properties of the incident radiation with the properties of specific optical materials to produce a microscopically detailed picture of the damage process. This understanding of the desorption dynamics leads to a valid description of damage from well below the plasma threshold up to and beyond that limit, and allows the identification of critical rate constants.

The Itoh classification of semiconductors and insulators hinges on an understanding of the ability of materials to support exciton formation, on the one hand, and relaxation to mobile, permanent electronic defects, on the other. The categories of materials together with representative substances which have these various features, are shown in Table I.

Table I

Category	Self-Trapped Excitons	Permanent Defects	Materials
I	No	No	Compound Semiconductors Some Metal Oxides
II	Yes	No	α -Quartz
III	Yes	Yes	Alkali Halides Alkaline-Earth Halides Fused Silica Other Metal Oxides (Alumina, Titania)

All of the materials in this Table are in fact either insulators or semiconductors, reflecting the fact that, in the typical laser environment, all materials, including metal mirrors and metal layered structures, are covered either with an oxide or with some other coating due to the presence of air or the laser environment, which renders the surface an insulator or, at best, a

semiconductor. It is interesting to note that virtually all optical materials of current interest in short wavelength laser designs fall into either category 2 or 3, forming self-trapped excitons or permanent defects or both.

We have seen that the alkali halides exhibit efficient ESD and PSD through the Pooley-Hersh defect-induced desorption mechanism. Materials in classes II and III of the Itoh taxonomy—which include virtually all interesting SWL optical materials—are particularly vulnerable to optical damage because they as a class, can participate in a variety of similar processes. In theory, materials in class I which forms neither self-trapped excitons, nor permanent defects, should be relatively invulnerable to electronically stimulated desorption and erosion of the type we have been considering. However, there is evidence [18] that the compound semiconductors are in fact etched or eroded to a significant degree by electrons and photons or by reactive ions, particularly in the presence of ultraviolet light. This probably means that the Itoh classifications scheme, while helpful, is not yet sufficiently differentiated to account for all the factors which contribute to optical damage. For example, since the Itoh scheme is based on bulk properties of materials, it fails to account for surface states, which are increasingly being implicated in optical damage processes [18]. Therefore, while we shall consider the Itoh taxonomy as a guide to the general phenomenology of electronically-induced optical damage, it is only that at present. In particular, it has little predictive power for extracting rate constants.

4.2. The Protective Overlayer

In early electron stimulated desorption experiments on alkali halides, it was found that samples prepared in air and then inserted into the ultra-high vacuum system only exhibited neutral alkali desorption after lengthy irradiation by the electron beam, even when the target was heated to very high temperatures in an ultra-high vacuum environment. Even sputtering by modest doses of noble gas ions failed to produce a virgin surface yielding neutral alkali atoms under electron stimulated desorption. It was not until detailed spectral scans throughout the visible region of the spectrum were taken that it became clear that desorption was in fact occurring, but not desorption of the alkali halides until some significant radiation damage had been done to the surface.

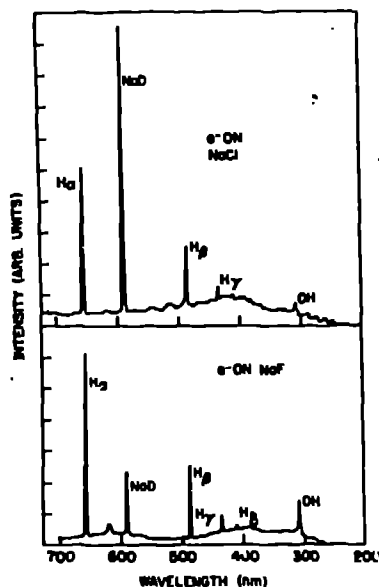


Figure 9 shows a pair of pictures showing electron stimulated desorption on sodium fluoride and sodium chloride. In this experiment the electron beam energy was held fixed while the visible spectrometer (Figure 3) was scanned through the range of wavelengths indicated on the horizontal axis. The various peaks in the desorption spectrum were identified from the atomic lines of various elements. In addition to the sodium line, there appears a virtually complete hydrogen spectrum (Balmer series), as well as lines from OH radicals and from a quasi-molecular structure whose exact nature is still under investigation [19]. The crucial item from the standpoint of optical damage is that, in the case of sodium fluoride, the relative yield of sodium is smaller than that of the hydrogen and other contaminant peaks, while in the case of sodium chloride, the sodium yield exceeds that of the contaminant species.

Fig. 9. ESD of Na^0 from NaF and NaCl in a hydrogen atmosphere. The electron energy was approximately 500 eV.

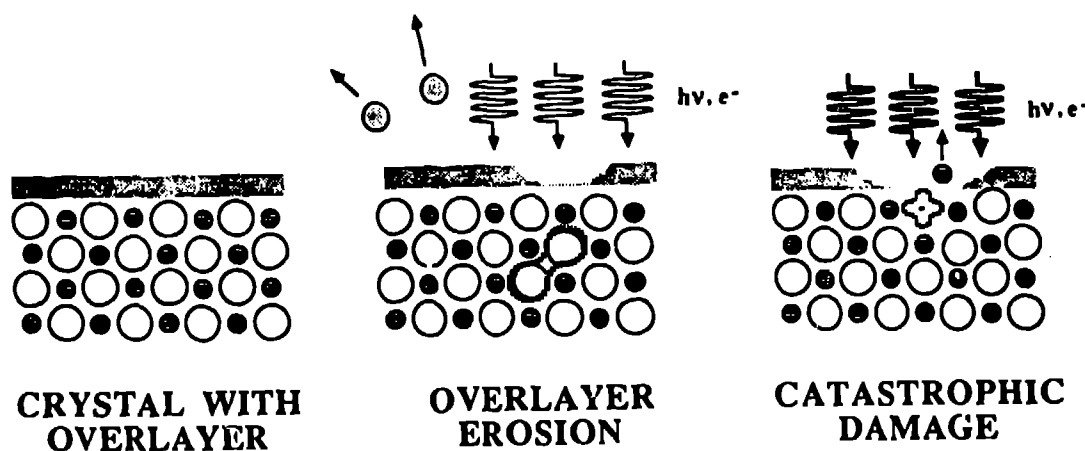
This implies that the surface overlayer and the binding of the overlayer to the substrate determine the rate at which substrate material will be ejected by electron irradiation. Similar results have been achieved in preliminary experiments in photon stimulated desorption at the Synchrotron Radiation Center of the University of Wisconsin. One of the tantalizing questions for further research is the extent to which this surface overlayer can be deliberately deposited on an optical surface in such a way that it does not affect the optical properties of the surface, but does influence the rate at which substrate material can be eroded through electron or photon bombardment.

Transition from Electronically to Thermally Induced Optical Damage

Using the DIET mechanisms in alkali halides as a model, and considering the effect of the surface overlayer, we now present a model of damage to short wavelength optical materials which takes account of electronically-induced changes in the structure and the composition of the material surface, and of the thermal effects which arise for laser intensities well above the plasma formation limit. In this model, we assume that a Pooley-Hersh type mechanism is operative in a substrate material of Type III, and assume that there is a protective overlayer which erodes at a rate significantly lower than the substrate material. The general scheme for this model is shown in Figures 10a, b, and c.

In Figure 10a, short wavelength laser or other irradiation is incident on an optical element with a protective overlayer and a substrate material forming both self-trapped excitons and permanent electronic defects. In Type III materials, defects produced in the substrate bulk are "getterd" to the interface between the overlayer and the substrate, forming a metallic interlayer. In the early phases of irradiation this metal-rich layer has no effect other than to present a thermal absorption site slightly below the surface of the optical element. It should be noted however, that in multilayer dielectric films, especially where the materials contain metals, it is likely that the existence of these interlayers may lead to serious thermal consequences in the catastrophic phase of laser damage.

In Figure 10b the irradiation has gone on sufficiently long or at sufficient intensities that the protective overlayer has begun to erode, exposing to subsequent irradiation the metal rich interlayer created during the precursor phase. Efficient creation of additional defects, in the near surface bulk and diffusion-dominated migration to the breach in the protective overlayer begins to occur. It should be noted that the precise location of the breacher or gaps in the protective overlayer will be determined by a number of random events, including, but not limited to: (1) the statistical migration of defects formed in the surface overlayer creating vacancies and under coordinated lattice in the overlayer; (2) surface rearrangements and reconstruction induced by desorption of materials at the surface of the overlayer and (3) the migration of metals from the interlayer into the surface overlayer, producing defects and under-coordinated sites in the lattice structure of the overlayer. Such processes can occur both in crystalline and in amorphous materials; in amorphous materials, the irregularities in the local electron densities simply means that it becomes more difficult to predict the sites at which defects or vacancies will eventually or temporarily come to rest.



By far the richest phenomenology and the most damaging events occur with the arrival of a laser pulse on a surface which has gone through the evolutionary phases indicated in Figures 10a and 10b. When the density of metallic atoms is sufficiently high that small agglomerations of metal have actually formed in the breached areas of the overlayer, it is possible for an intense laser pulse to create a metallic plasma, since agglomerations of even only a few tens of atoms already have essentially metallic properties [20]. The electrons accelerated in the laser field

can be efficient for electron-stimulated-desorption with near unit efficiencies, ejecting atoms or molecules from the optical material. The ions accelerated in the plasma by the laser field are even more damaging since, at relatively low energies, they have sputtering efficiencies greater than unity and produce significant desorption, erosion and cratering of the surface. The acceleration of ions and electrons also produces ultraviolet radiation which can cause photon stimulated desorption. And, finally, the absorption of light in the metal-rich overlayer will also produce thermal cratering and damage typical of the phenomenology already well-known at infrared laser wavelengths.

Thus beginning with a picture of individual desorption events initiated by the deposition of electronic energy, we have come full circle to the situation where catastrophic damage is produced both by plasma formation and by thermal absorption at the surface. It is important to understand, however, that while the ultimate damage effects may be thermal in nature, and could perhaps at this stage even be described by a thermal model, the correct description of the microscopic physics (including the determination of the critical rate constants) hinges on understanding electronically stimulated processes induced by short wavelength laser photons, and by hard ultraviolet photons and energetic electrons from the laser pumping process. Moreover, while we have not mentioned surface chemistry explicitly, we should not overlook the fact that reactive ions in the laser plasma, together with metastable neutral species and superthermal atoms from the laser plasma, will also work destructive mischief at the surface.

5. Conclusions

We have argued that DIET processes are likely to be the primary cause of damage to optical materials at short laser wavelengths, say, below 400 nm. The evidence for this point of view rests on a growing body of experimental data from which we are rapidly building a detailed atomic-scale picture of the dynamics of desorption processes. While the materials studied-the alkali halides are not the specific choices in most SWL's, they are representative of a generic class of wide band-gap insulators which support the creation of self-trapped excitons and relaxation to permanent defects. Because so many SWL optical materials fall into this class, the generic predictions of our damage model should hold true, although the desorption rates (or efficiencies) may well be different in, say, the alkaline-earth halides or metal oxides than in the alkali halides we have studied.

The key steps in the damage process, based on the experimental evidence, are:

- (1) the formation of defects on the surface and in the near-surface bulk;
- (2) changes in surface and near-surface composition (formation of a metal rich overlayer) due to the thermally-driven migration of these defects; and
- (3) the occurrence of catastrophic plasma formation leading to self-reinforcing desorption and sputtering processes.

While we have concentrated on processes occurring on the near-surface bulk due to relatively high-energy electrons and photons, there is also evidence implicating long-lived surface states in the desorption of excited neutral atoms. Should the photon-energy thresholds for reaching these states prove to be sufficiently low, it would make possible the triggering of DIET processes by low-energy laser photons in efficient, single-photon excitations.

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